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Atmospheric toluene and benzene mole fractions at Cape Town and Cape Point and an estimation of the hydroxyl radical concentrations in the air above the Cape Peninsula, South Africa.

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ABSTRACT

Benzene and toluene, emitted into the atmosphere from a number of common anthropogenic activities, pose a significant human health risk. The mole fractions of toluene and benzene were measured at two urban locations (Foreshore and Potsdam) in Cape Town and one background site at Cape Point, South Africa over the period of July-November 2017. The analysis of the mole fractions of benzene and toluene at two sampling sites in the city of Cape Town gave an indication of the probable anthropogenic sources of the air masses sampled at these sites. We propose that a traffic source dominated at the Foreshore site, while industrial processes dominated at the Potsdam site. The analysis of wind rose plots of benzene and toluene and the elevated mole fractions observed at the remote “clean air” sampling site, Cape Point, suggest that polluted air from Cape Town is the major source of the benzene and toluene mole fractions observed at Cape Point. Hydroxyl (OH) radical concentrations were estimated for Cape Town from the difference in T/B ([toluene]/[benzene]) ratios between Cape Town and Cape Point. The Cape Town OH estimations displayed a mean of $(7.2 \pm 3.5) \times 10^6$ molecules cm^{-3} at the Foreshore site and $(9.1 \pm 4.4) \times 10^6$ molecules cm^{-3} at the Potsdam site, without consideration of dilution reducing to $(5.4 \pm 3.4) \times 10^6$ molecules cm^{-3} for the Foreshore site and $(7.4 \pm 4.6) \times 10^6$ molecules cm^{-3} for Potsdam site for the period of July-November 2017 when dilution was considered. The estimated Cape Town OH concentrations are on the high side, but consistent with the results from other urban studies and may suggest a role for OH recycling following biogenic emissions between Cape Town and Cape Point.

INTRODUCTION

Aromatic volatile organic compounds (VOCs) play a crucial role in the formation of photochemical smog in polluted air.^{1,2} In urban areas, the monoaromatic VOCs such as benzene and toluene are important pollutants, contributing a significant proportion to non-methane VOC total mole fractions.³ The emission of benzene and toluene into the atmosphere occurs mainly from the evaporation and combustion of petroleum products. Further emissions result from the use of benzene as a chemical intermediate and/or solvent in the production of many foams and pesticides and toluene as a common industrial solvent.⁴ The largest industrial use of toluene as a solvent is in the paint and coating industry followed by inks, adhesives, the leather and pharmaceutical industries. Toluene is also used directly in several consumer products (e.g. sanitizing agents, household aerosols, varnishes, paint thinners and antirust preservatives).⁵ The contribution of natural sources of benzene, which include volcanoes and forest fires, to atmospheric mole fractions of this compound, are relatively minor when compared with anthropogenic sources.^{6,7}

The negative health impacts of benzene have been widely studied. Benzene is a well-established carcinogen, depressing bone marrow formation and initiating the onset of leukaemia,⁸⁻¹¹ and inducing DNA damage in children and outdoor workers.¹² Toluene, while less of a health risk when compared with benzene, causes drowsiness and dizziness at low concentrations and damage to the nervous system at high concentrations.^{13,14} Therefore, given the health risks associated with inhaling these two compounds, it is important that the levels of tropospheric benzene and toluene are continually monitored. In addition, as air pollutants, benzene and toluene contribute to the formation of tropospheric ozone, and a recent study¹⁵ showed that the total contribution of benzene and toluene, to photochemical ozone production along the Trans-Siberian Railway, was about 16%

compared with that of isoprene's contribution. Not unexpectedly, given the significant role of anthropogenic pollution sources on regional ozone photochemistry and air quality, the contribution of benzene and toluene was found to be significantly higher in urbanized areas along the railway.

The photochemical production of O_3 from VOCs in the atmosphere has been well described.¹⁶ The atmospheric lifetimes of benzene and toluene are defined by reactions with hydroxyl radicals (OH), which has also been shown to be the primary removal pathway.^{17,18} The mean atmospheric lifetimes of benzene and toluene, with respect to OH, have been shown to be 9.4 and 1.9 days, respectively.¹⁹ During summer, higher atmospheric OH concentrations decrease the mole fractions of benzene and toluene in tropospheric air relative to winter mole fractions.

Benzene and toluene are often co-emitted into the atmosphere with source dependent toluene to benzene ratios, [toluene]/[benzene] (T/B). Previous studies have shown that traffic emissions have a T/B ratio in the range of 1 – 3,^{20–22} while industrial processes exhibit a T/B ratio of > 3 .¹⁵ Toluene reacts with OH more rapidly than benzene,¹⁸ decreasing the T/B ratio.¹⁵ Therefore, measurements of benzene and toluene can be used to determine the degree of photochemical aging that has occurred between a sampling site(s) near their source and another sampling site(s) further away.²³

Globally, numerous studies of the mole fractions of benzene and toluene and T/B ratio have been reported.^{15,20,24–34} However, there is a paucity of information about atmospheric mole fractions of benzene and toluene in South Africa. This study aims to investigate the variations in benzene and toluene mole fractions in the surface air over Cape Town and Cape Point. The Cape Point sampling site is removed from known sources of benzene and toluene (e.g. traffic and heavy industry). Dependent on the wind direction, Cape Point either receives well-mixed marine air from the South Atlantic or anthropogenically polluted air masses from the city of Cape Town.³⁵ Thus, the analysis of the T/B ratios in this comparative study can first give an indication about the types of emission

sources in the city of Cape Town and second, provide an estimate of OH concentrations in the air above the Cape Peninsula and False Bay, South Africa.

The atmospheric lifetime of OH is extremely short ($\tau(\text{OH}) \sim 0.01\text{-}1\text{ s}$) and concentrations are low ($\sim 10^6\text{ molecules cm}^{-3}$) making it difficult to measure directly.¹⁶ The OH concentrations in major urban areas are reported to be $(2.1 - 9.0) \times 10^6\text{ molecules cm}^{-3}$.^{16,36} OH concentrations have been estimated using a number of methods, including measuring the changes of the T/B ratio between two sites.^{37,38} In the study, we have estimated the atmospheric OH concentrations over False Bay and the Cape Peninsula using the T/B ratio.

EXPERIMENTAL

MEASUREMENT LOCATIONS

Concurrent measurements of benzene and toluene mole fractions were recorded at two urban sites in the City of Cape Town (CT): Foreshore (FS: 33.9° S, 18.4° E) and Potsdam (PD: 33.8° S, 18.5° E) and at one background site, Cape Point: (CP: 34.5° S, 18.2° E) between July and November 2017. The FS monitoring station lies between Cape Town's shipping harbor and highly congested major traffic highways (N1 and N2) entering the city (Figure 1). The PD monitoring station is positioned in an industrial area, adjacent to the only major oil refinery in Cape Town. In addition, it is located in close proximity to one of the national highways (N7), from Cape Town to Namibia, and opposite to a major road (Koeberg Rd, Tableview - see Figure 1). The Cape Point Atmospheric Watch station provided an appropriate site, 60 km southeast of Cape Town, to provide background measurements of benzene and toluene in the atmosphere over the Cape Peninsula.

The Cape Point sampling site lies at the southern end of the Table Mountain national park (see Figure 1). More than 1 million tourists visit the park each year, who travel to Cape Point either by

car or bus. The traffic terminates in a parking area 0.5 km away from and 150 m below the sampling mast of the Cape Point GAW station. Although we recognize the possible impact of the traffic flow on the diurnal cycle, this impact is minimal because absolute measured mole fractions of benzene and toluene remained in the low parts per trillion (ppt) range.

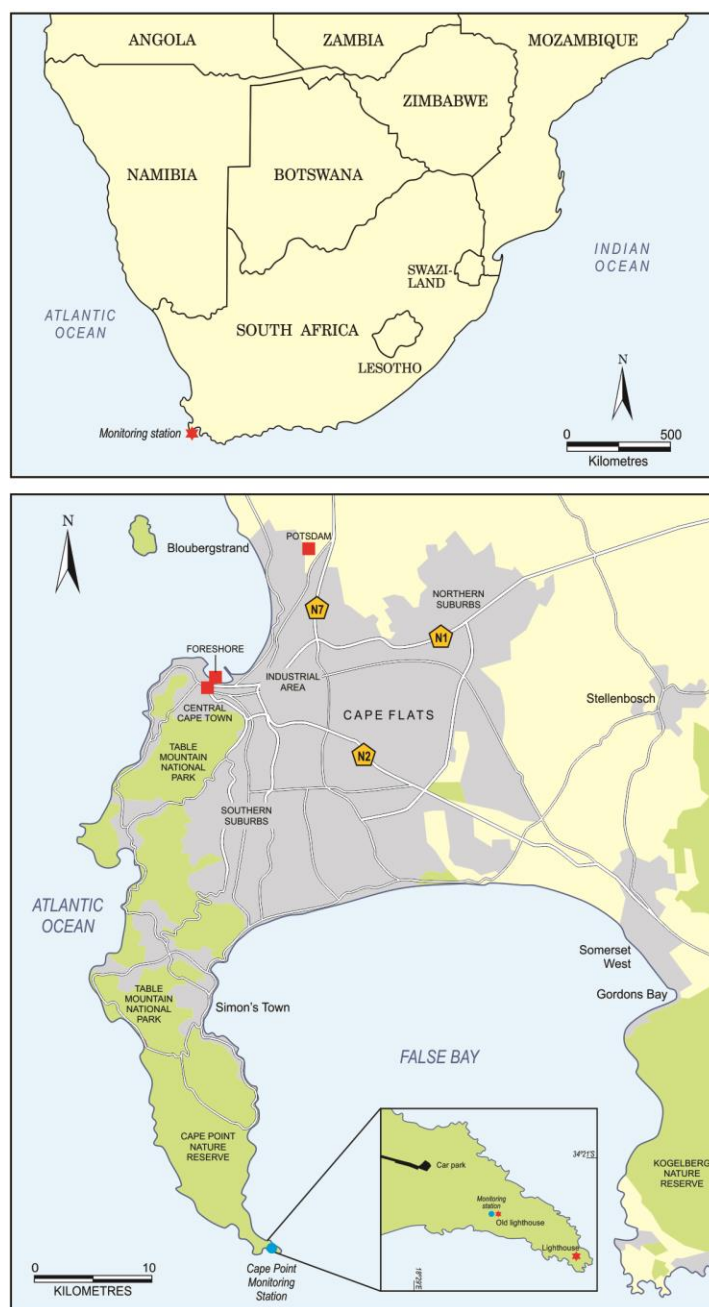


Figure 1: Map of the Cape Peninsula, South Africa indicating the positions of the Foreshore, Potsdam and Cape Point sampling sites in the city of Cape Town. Insert highlights the relative positions of the parking area and monitoring station at Cape Point.

MEASUREMENT TECHNIQUES

The benzene and toluene measurements at FS and PD were performed using a Syntech Spectras GC955 series BTX analyzer with a photo-ionization detector. A constant shelter temperature of $(25 \pm 5) ^\circ\text{C}$ is maintained within the City of Cape Town's air quality monitoring stations. These are small prefabricated structures, strategically located in prominent, permanent positions around the city. Each air quality station has a sampling manifold located between 3-15 m above ground level. A high flow pump draws air through the sampling manifold at $\sim 10 \text{ l min}^{-1}$ creating a bulk flow. A secondary gas stream for analysis was drawn from the bulk flow at a maximum of 1.5 l min^{-1} for 15 min.

An indirect piston system was used to draw a 35 ml sample from the secondary gas stream. This sample was injected onto a Tenax GR thermal desorption trap at $-5 ^\circ\text{C}$ for pre-concentration. Following trapping, the sample was thermally desorbed at $180 ^\circ\text{C}$ and injected directly onto the AT264 capillary column ($15 \text{ m} \times 0.32 \text{ mm ID} \times 1.8 \text{ } \mu\text{m}$ film thickness). The oven was maintained at an isothermal temperature of $60 ^\circ\text{C}$ and back flushed prior to the subsequent sample introduction. A nitrogen carrier gas (grade 5.0), at a flow rate of 6 ml min^{-1} , was maintained through the system. Benzene and toluene were detected by a photoionization detector (PID) with a sensitivity range of 0.03 – 300 ppb and precision of $<3\%$ at 1 ppb. The calibration of the system was typically

performed through an external standard 6-point curve within a range of 4 to 100 ppb. A total cycle time of 15 min was achieved on this system. The samples were averaged to one per hour.

An Agilent (6890/5973) gas chromatograph-mass spectrometer (GC-MS) with a custom adsorption desorption system (ADS) was used to measure benzene and toluene at Cape Point. Further details about the instrumentation can be found in Simmonds et al.³⁹ and Kuyper et al.⁴⁰ Here we present a short summary of the sampling method and calibration details relevant to these compounds. Atmospheric samples (2 l) were preconcentrated at -50 °C on a thermal desorption microtrap composed of Carbotrap B (3 mg), Carboxen 1003 (5 mg) and Carboxen 1000 (4 mg).^{41,42} The trapped samples were desorbed at 240 °C through direct Ohmic heating of the trap and injected directly on to the column (J&W Scientific CP Sil-5, 100 m × 0.32 mm ID × 5 µm film thickness). A constant flow of helium carrier gas (Air Liquide Grade 5.0) of 1.8 ml min⁻¹ was maintained through the column for the separation of the compounds. Air samples were analyzed once every four hours. The calibration of the GC-MS for benzene and toluene was performed through the repeated injection of a short-term working standard, alternate to each atmospheric measurement. The short-term working standard, a locally filled cylinder (Essex 34 l), was calibrated fortnightly against a long-term standard cylinder (Essex 34 l) filled and calibrated at Mace Head, Ireland. Toluene mole fractions were assigned at Mace Head from the EMPA preliminary scale and benzene from the University of Bristol preliminary scale at Mace Head. The residual standard deviation precision for the GC-MS was 2% for both benzene and toluene measurements at Cape Point.

The two instruments in the City of Cape Town network were calibrated against the same external standard (Air Liquide, 100 ppb mixture). The calibration of the City of Cape Town instruments was conducted by Envirocon Instrumentation (<https://www.envirocon.co.za/>). Any offset between

the instruments was performed through the calibration. Any systematic biases between the systems used by the City of Cape Town and the Cape Point were tested through a comparative study. Air samples were captured in 0.8 stainless steel flasks by means of metal bellows pump, concurrently while samples were being analysed at the Foreshore site. The captured air samples were subsequently analysed on the GC-MS system at Cape Point later that day. A total of 9 standard sample runs were conducted in a day. A negligible offset (<1%) was applied to these data. Furthermore, since the OH concentration estimation relies on the ratios of T/B and not the absolute values. The absolute values are therefore not critical for that portion of the study.

ESTIMATION OF HYDROXYL RADICAL CONCENTRATIONS

The atmospheric concentrations of OH radicals were estimated from comparison of the T/B ratios at FS and PD compared with those at Cape Point. The OH concentrations were determined for air mass parcels that traveled from Cape Town to Cape Point. In this simplified study, it is assumed that the air parcels travel directly from Cape Town to Cape Point. The only mechanism leading to the depletion of toluene relative to benzene (decrease in the T/B ratio) is through oxidation with OH radicals. In the first instance, no mixing and dilution is considered in the analysis. A subsequent modification estimates the amount of atmospheric mixing and dilution with clean air before arriving from Cape Town to Cape Point and was approximated using the NAME dispersion model. A complete description can be found in the supplementary information. A simple footprint was applied dividing particle history into two sectors (see Figure S3) and the NAME model then returned the number of particles arriving at Cape Point from the two sectors (that likely to be affected by Cape Town air and that which is likely to be clean and have little or no residual benzene and toluene). Inclusion of an estimate in dilution reduces the initial [OH]

returned and therefore we suggest that the initial estimate without dilution is considered an upper limit. The initial ratios of T/B derived from measurements at FS and PD are assumed to be representative of Cape Town air and the first calculation assumes that there is no entrainment of these compounds en route to Cape Point. It is already noted that the assumption that entrainment is zero along the transit from Cape Town to Cape Point will result in an overestimation of OH concentrations, leading to an upper limit. However, we know that Cape Point is a clean air site and that are sampled will be a mixture of Cape Town influenced air and that from clean (ocean) sectors where little or no Toluene and Benzene are present. We will discuss the [OH] calculation next, but dilution with clean air will reduce the T/B ratio and return a larger [OH] than is really in operation between Cape Town and Cape Point and so in the revised calculation, we correct for this dilution.

The OH concentrations were estimated following the photochemical clock equation reported in Warneke et al.³⁷

$$[\text{OH}] = (\ln(\text{T/B})_{\text{CP}} - \ln(\text{T/B})_{\text{CT}}) / t(k_{\text{B}} - k_{\text{T}}) \quad (1)$$

In equation 1 the concentration of hydroxyl radical [OH] is reported in molecules cm^{-3} , $(\text{T/B})_{\text{CP}}$ is the ratio of T/B for Cape Point (CP) and $(\text{T/B})_{\text{CT}}$ is the ratio of [toluene]/[benzene] for Cape Town (CT), t is the transit time in seconds and k_{B} ($7.57 \times 10^{-12} \exp(-529/T) \text{ cm}^3 \text{ s}^{-1}$) and k_{T} ($2.09 \times 10^{-12} \exp(322/T) \text{ cm}^3 \text{ s}^{-1}$) are the temperature dependent rate coefficients for the reaction with OH of benzene and toluene respectively, taken from Atkinson.¹⁸ Low resolution (2.5° horizontal resolution), forward from Cape Town and backward from Cape Point, HYSPLIT trajectories were used to estimate a mean air parcel time between the sites. A mean transit time for an air mass from Cape Town to Cape Point was estimated to be nine hours (32400 s). This mean estimated transit time was used for all the samples analyzed. Variations in the transit time would obviously result

in different OH concentration estimates, with shorter transit times producing higher OH concentrations and vice versa. The current uncertainty in estimating the transit time for each sample is a limitation of this study. However, using the fixed time as described here provides a reasonable first estimate of OH concentrations over the Cape Peninsula.

The sensitivity of equation 1 to variations in temperature was tested by maintaining a constant transit time (9 hours) while varying the temperature (270 - 300 K). The temperature variation induced no significant variability (Figure S1) in the estimated OH concentrations ranging between 4.2×10^5 molecules cm^{-3} to 1.3×10^7 molecules cm^{-3} and 1.0×10^6 molecules cm^{-3} to 1.8×10^7 molecules cm^{-3} for FS and PD, respectively (270 - 300 K) for the analysis with dilution. The air temperature at Cape Point displayed a mean of 288 ± 3 K (Figure S2), thus a standard temperature of 290 K was used in the final estimate of [OH].

RESULTS AND DISCUSSION

CAPE TOWN BENZENE AND TOLUENE

The measurements of benzene and toluene from FS and PD, during July to November 2017 showed that the mole fractions were principally < 2 ppb for benzene and < 5 ppb for toluene with numerous extreme events where the mole fractions rose to a maximum of 6 and 15 ppb, respectively (Figure S4). Generally, the mole fractions of both benzene and toluene at the PD site were found to be larger than those observed at FS. The average mole fractions for the period of July-November 2017 were calculated for benzene as 1.24 ± 1.09 ppb (PD) and 0.76 ± 0.69 ppb (FS), and for toluene as 4.32 ± 2.90 ppb (PD) and 2.10 ± 2.07 ppb (FS). The mean and range of the benzene and toluene mole fractions observed here compare favorably with reported literature from some other urban areas (Table 1)

Table 1. Comparison of some reported benzene and toluene mole fractions from various cities around the world. Mole fractions reported in ppb, except for Cape Point which is reported in ppt.

City	Site dominated by	Benzene	Toluene	Reference
Cape Town FS, South Africa	Traffic	0.76 ± 0.69	2.10 ± 2.07	This study
Cape Town PD, South Africa	Industrial	1.24 ± 1.09	4.32 ± 2.90	This study
Cape Point, South Africa	Marine	27.41 ± 46.33 (ppt)	61.96 ± 166.0 (ppt)	This study
Algiers, Algeria	Traffic	0.61	1.21	⁴³
Helsinki, Finland	Traffic	0.66 (0.41-1.0)	1.75 (1.14-3.34)	⁴⁴
Helsinki, Finland	Industrial	0.30 (0.09-0.47)	0.72 (0.34-1.51)	⁴⁴
Yokohama, Japan	Industrial	0.72 (0.38-1.13)	4.62 (1.23-8.95)	⁴⁵
London, UK	Traffic	1.06	2.16	⁴⁶
Middlesbrough, UK	Industrial	1.01	1.49	⁴⁶
Harwell, UK	Rural	0.38	0.60	⁴⁶
Bombay, India	Industrial	9.00	5.92	⁴⁷
Sao Paulo, Brazil	Traffic	2.6	9.0	⁴⁸
Macau, China	Traffic	10.92	22.79	⁴⁹
Nanhai, China	Industrial	6.26	10.37	⁴⁹
New Jersey, USA	High Urbanization	0.43	0.85	⁵⁰
New Jersey, USA	Low Urbanization	0.23	0.29	⁵⁰
La Coruña, Spain	Traffic and Industrial	3.12	7.41	⁵¹

Toulouse, France	Traffic	(0.22-1.19)	(0.80-3.74)	⁵²
Pamplona, Spain	Traffic	0.89	3.52	²⁷

Note: The maximum and minimum values are shown in bracket

The benzene and toluene mole fractions observed at both sampling sites in Cape Town displayed a variability of 1-2 ppb for benzene and as much as 10 ppb for toluene (Figure 2). This variability was occasionally sustained for a few days and up to a week. The (normalized) weekly cycle at PD showed a maxima on the weekend and a minimum on Wednesday (Figure 2c). These data have been normalized or transformed through the subtraction of the mean from each measurement. This has been done to fit the different measurements on a single scale. We propose that changes in the fuel and other petroleum production cycle at the neighboring refinery reflect this observed weekly cycle at PD. Diurnally, the benzene and toluene mole fractions at PD displayed a maximum between midnight and 2 am (for benzene) and midnight to early morning (for toluene) and a minimum in the mid-afternoon for both benzene and toluene, which is very consistent with the study of an industrial location of Yokohama, Japan.²⁹ These diurnal fluctuations may be related to either increased nocturnal refinery activity or decreased photochemical activity at night resulting in the accumulation of benzene and toluene. The T/B ratio at PD was consistently well above 3 (range 1 to 27, mean= 4.4 and mode = 4.0) which is consistent with industrial processes (Figure 2d).¹⁵ Diurnally the T/B at PD increased through the morning, peaking at 1 pm, then decreased through the afternoon. At no point in the diurnal cycle did the T/B ratio decrease below 4.

The weekly cycle of benzene and toluene at FS differs from that at PD, with peaks on Monday and Friday and a minimum on Tuesday-Wednesday (Figure 2a). In contrast to PD, the benzene and toluene mole fractions at FS displayed a bi-modal diurnal cycle with maxima at 6 am and 6

pm coincident with peak traffic flows entering and leaving the city center respectively (Figure 2b). The T/B ratios at FS were mostly below 3 (range 0.02 to 21.3, mean= 2.6 and mode = 2.0; Figure 2b). The strong diurnal and weekly cycle along with the low T/B ratio, suggests that the dominant source of benzene and toluene at the FS site is vehicular traffic. The occasional incidents of elevated T/B ratios > 3 (Figure 2b) may arise from the adjacent harbor where heavy fuel oil ships predominate (Figure S6). Both Cape Town sampling sites recorded multiple occasions when the T/B ratio rose to above 10 (Figure S4). These indicated elevated toluene mole fractions, which may suggest a significant, as yet unidentified, and intermittent local toluene source. Some light industries in Cape Town such as packaging, paper, plastics, timber and wood products, building construction, industrial equipment, machines, vehicles, textile and furniture may use toluene as solvent (Figure S7).

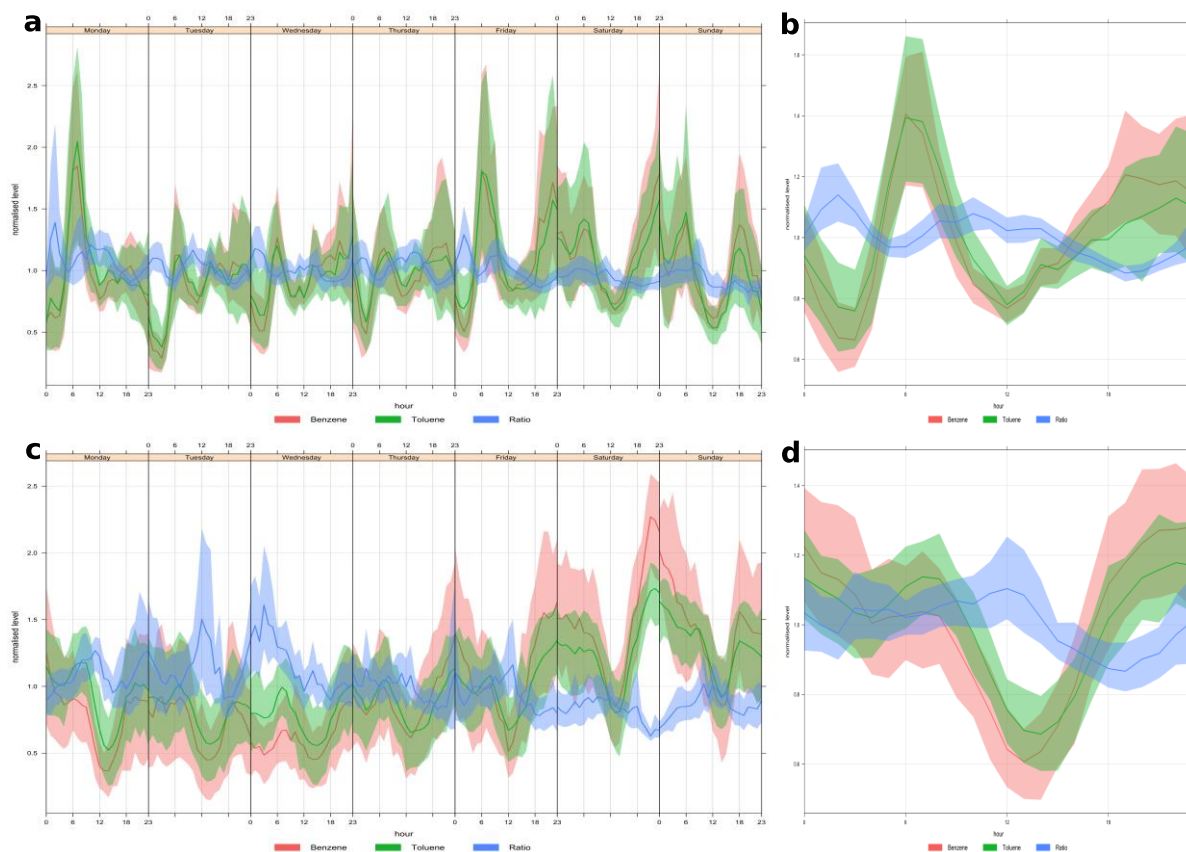


Figure 2. The normalized integrated weekly time series plots of benzene, toluene and the toluene/benzene ratio at the FS (a) and PD (c) sampling sites. Normalized diurnal cycles for the FS (b) and PD (d) sampling sites.

There was a strong correlation between benzene and toluene mole fractions at both FS and PD with Pearson r values of 0.95 and 0.94, respectively (Figure 3). These correlations strongly suggest that benzene and toluene have a co-located source. The relationship between the mole fractions of benzene and toluene at FS was linear with limited deviation, providing additional evidence of co-located (same) sources of these two compounds (Figure 3 (red points)). The benzene: toluene linearity observed here is consistent with a similar study over London.³³

Interestingly, the mole fractions of benzene and toluene at PD exhibited a non-linear relationship (Spearman's non-linear $r = 0.98$, Figure 3 (black points)). This suggests evidence of a strong source of benzene, which is not a source of toluene. The refinery is the most likely source of the observed benzene.⁵³ Regrettably, the refinery's 2017 product refining cycle was not accessible to the authors and so no further comment can be made.

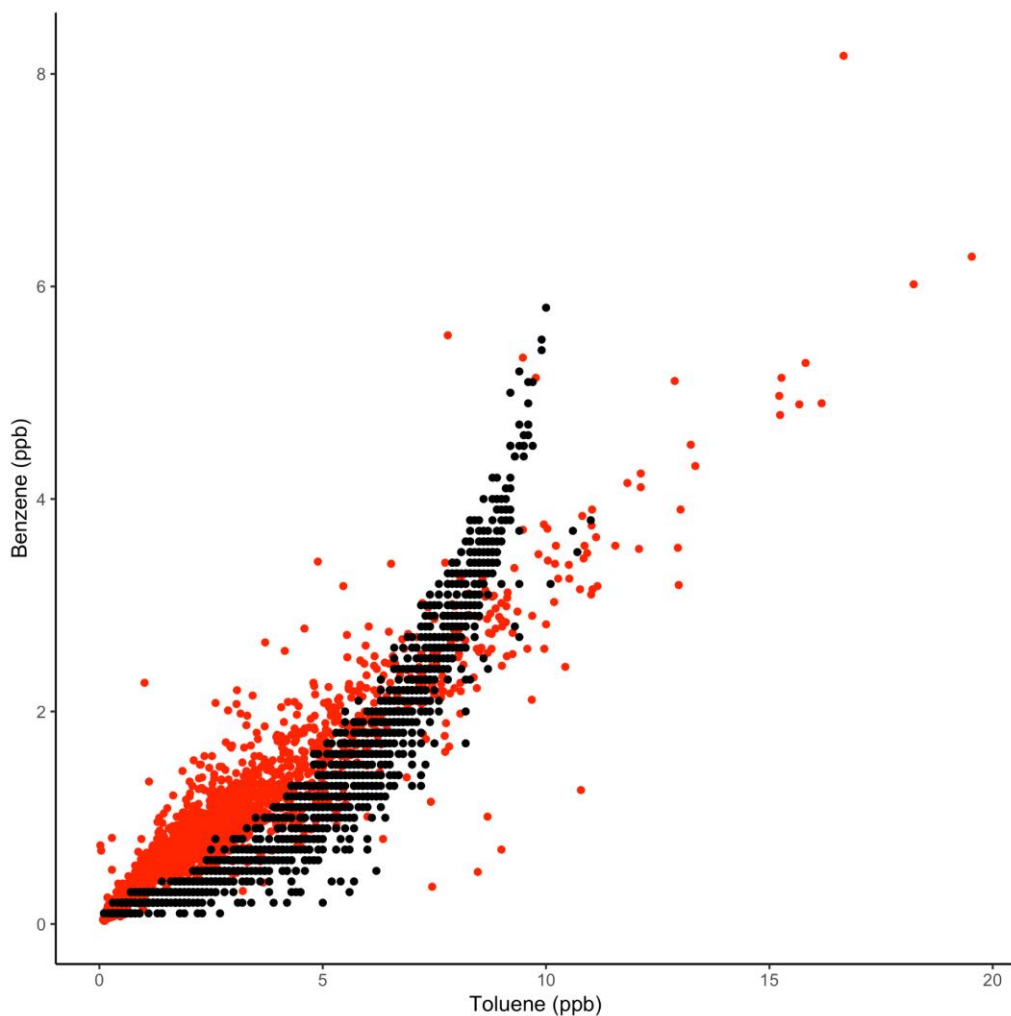


Figure 3. Relationships of toluene and benzene at FS (red) and PD (black).

CAPE POINT BENZENE AND TOLUENE RATIOS

The benzene and toluene mole fractions measured at Cape Point appear to have a common and consistent source from the north east, confirmed through a wind rose plot analysis (Figure 4). The Cape Point T/B ratios (range 0.2 – 34.8 and mean=1.6, Figure 4c) show a similar pattern to that observed in Figures 4a and 4b. From the wind rose plots it is apparent that, other than from the north east, i.e. Cape Town, there were no additional significant sources of the benzene and toluene measured at Cape Point. The few samples that arrive from other wind directions may simply be recirculation of air masses. Given that toluene has a shorter atmospheric lifetime than benzene, the

T/B ratio decreases as air samples are photochemically aged through reaction with OH. Figure 4c indicates, not unexpectedly, that there is no observable toluene and benzene source to the south of Cape Point, in the South Atlantic clean air sector (120-320°). The highly elevated T/B ratios observed may be an artifact of a local source of toluene that is not a source of benzene at Cape Point. 1-day back trajectories simulated by the NAME (Numerical Atmospheric dispersion Modelling Environment) model analysis of air mass histories for the lowest and highest 5% of T/B ratios measured at each of the measurement sites are shown in Supplementary Figures S9-S11. Whilst not definitive, they illustrate that the highest T/B ratios at Cape Point are associated with Cape Town sources and the lowest T/B ratios occur predominantly from a maritime source. At both urban sites, air masses associated with clean air origins return lower T/B ratios. This analysis lends weight to the assumption that elevated benzene and toluene measured at Cape Point is predominantly from Cape Town and its environs.

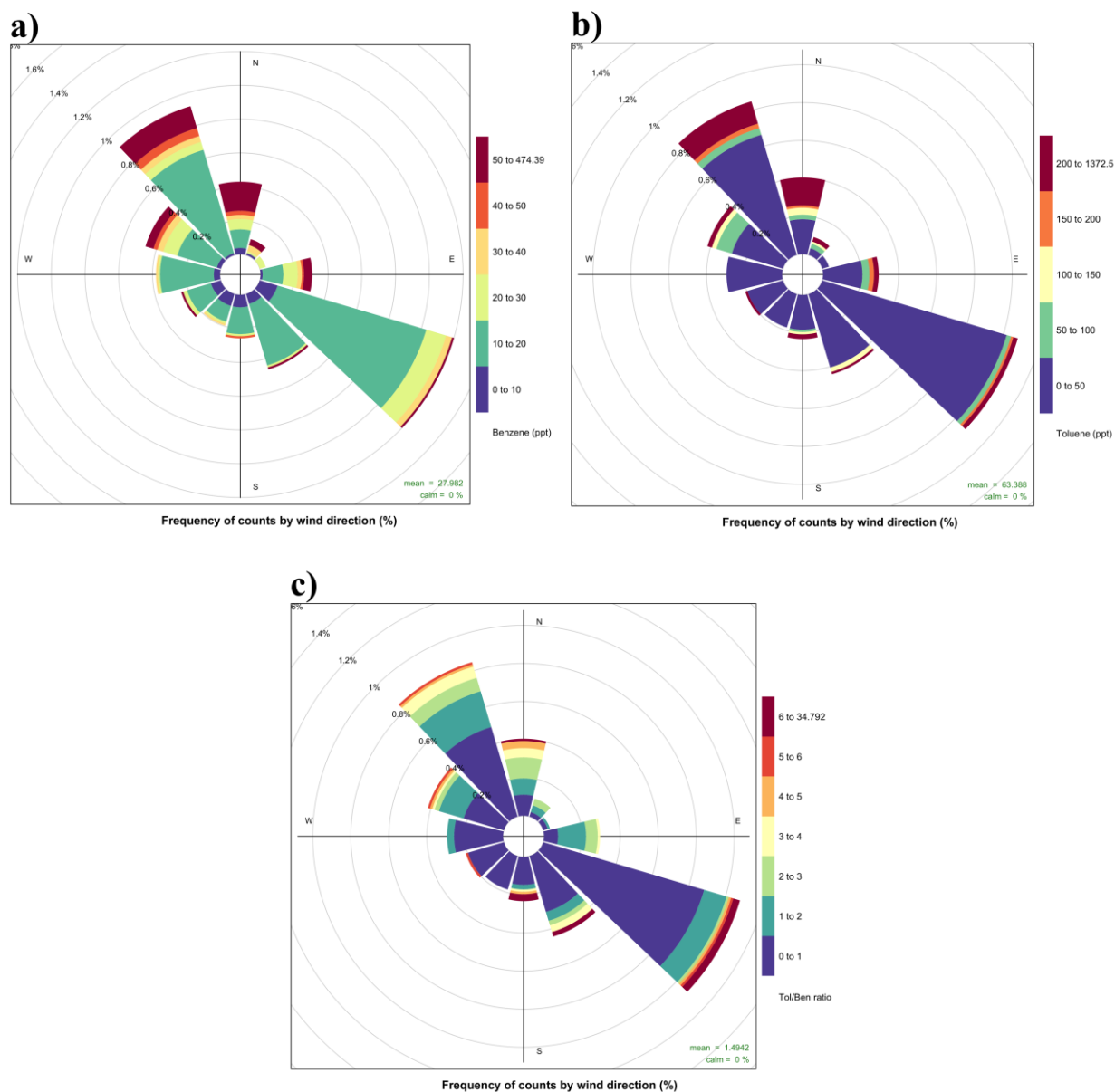


Figure 4. Wind rose plots for benzene (a), toluene (b) and T/B ratio (c) for Cape Point as a function of both wind speed and direction integrated over July–November 2017.

The benzene and toluene mole fractions at Cape Point were in the low ppt range, an order of magnitude lower than those of the city of Cape Town. The variability in the measurements were much larger with a mean of mole fractions of 27.41 ± 46.33 ppt and 61.96 ± 166.00 ppt for benzene and toluene, respectively. Occasional, highly elevated benzene and toluene mole fractions as much

as twice the mean, were observed (Figure S5). These observations were coincident with moderate to strong northerly winds and account for 22% and 33% of the samples for benzene and toluene, based on an interquartile range outlier (IQR) method. The IQR is defined as the difference between the 75th and 25th percentiles. This range is multiplied by 1.5 and either added to or subtracted from the 75th or 25th percentiles. Any values outside the IQR*1.5 values are marked as outliers.⁵⁴ A locally consistent baseline was observed with occasional, large departures as seen in the weekly cycle (Figure 5a). The diurnal cycle showed a bi-modal distribution for the benzene and toluene mole fractions (Figure 5b). Similar to FS, there was a mid-morning peak followed by a second peak at approximately 18:00 local time. Generally, the T/B ratios calculated for Cape Point display a low value within the range of 1-3, with occasional elevated points and periods. Although we recognize vehicular traffic as a source of benzene and toluene, the car park at Cape Point does not influence the observed mole fractions. The mole fractions observed remained in the low ppt range, suggesting a remote source. There is no strong evidence from the diurnal cycle of increased traffic (Figure 5b). We would expect a strong relationship between the benzene and toluene mole fractions and carbon monoxide at Cape Point ($r = 0.33$ and 0.29 respectively), if the hydrocarbon emissions were associated with vehicular traffic. The parking area at Cape Point is small and removed from the sampling site (0.5 km and 150 m below). The microclimate around Cape Point results in isolating the sampling site from the car park (Ernst Brunke, Pers. Comm.). Any entrainment is therefore negligible and does not influence the observations reported here.

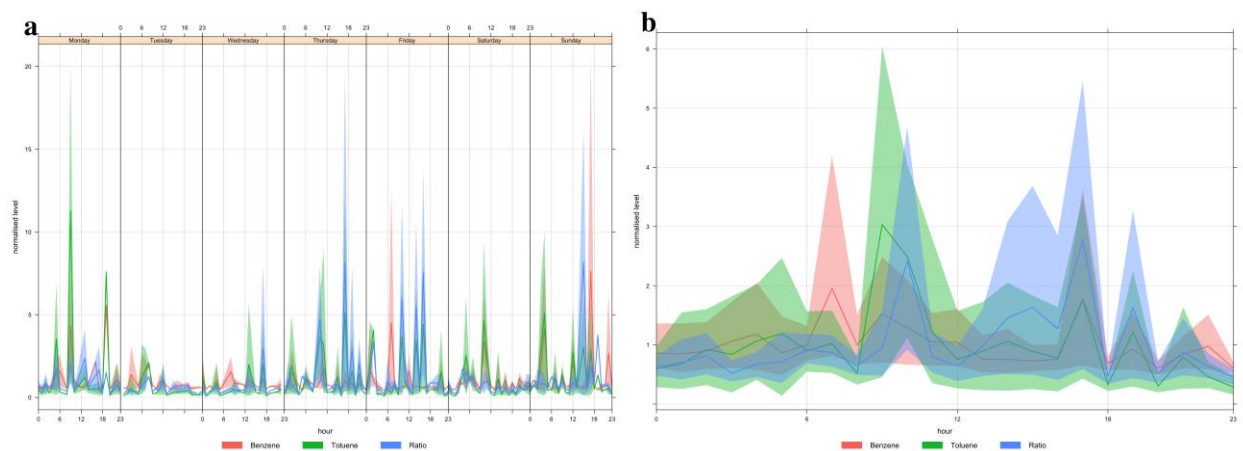


Figure 5. Normalized weekly time series (a) and diurnal cycle (b) plots of benzene, toluene and the T/B ratio at Cape Point.

ESTIMATION OF OH CONCENTRATIONS

The estimated OH concentrations for the Cape Peninsula were calculated from the T/B ratios at FS and PD compared with Cape Point (Figure 6). Prior to analysis, the dataset was sorted by wind direction at Cape Point to include only continental air from Cape Town. Sample times were subsequently matched over the transit time prior to the analysis. Each corresponding matched sample was then analyzed individually, generating an estimate of OH concentration for FS and PD. The mean OH concentrations estimated for the Cape Peninsula under the fixed transit time conditions were found to be $(7.2 \pm 3.5) \times 10^6$ molecules cm^{-3} and $(9.1 \pm 4.4) \times 10^6$ molecules cm^{-3} from the FS and PD T/B ratios, respectively without considering dilution. Using NAME model derived particle counting, the dilution factor can be estimated and using the modified value for $\ln(\text{T/B})_{\text{CP}}$ that takes dilution into consideration (see supplementary information), we arrive at $(5.4 \pm 3.4) \times 10^6$ and $(7.4 \pm 4.6) \times 10^6$ molecules cm^{-3} for the mean OH concentrations for the FS and PD sites, respectively. These results are comparable with other studies,¹⁶ who reported OH

concentrations in different environments within the range of $(1.0 - 9.0) \times 10^6$ molecules cm^{-3} with a mean of 5.0×10^6 molecules cm^{-3} . Interestingly, the estimated 2017 OH concentrations for the two sampling sites in Cape Town displayed some variability toward the end of the austral winter and the onset of spring in 2017, with a minimum in August (for both sites) and a maximum in September (Figure 6). The range and variability of the estimated OH concentrations are likely driven by variations in the benzene and toluene source strength and physical atmospheric processes. The emission strength or mole fractions at the sources influenced by variations in traffic and industrial processes and diurnal and synoptic conditions such as variations in the boundary layer height and wind strength will result in local variations in the source strengths. These processes combined will lead to the observed variability in the estimated OH concentrations. It is known that Criegee Chemistry following ozonolysis of alkenes can supplement production of OH and may play a role in the nocturnal OH estimates.⁵⁵

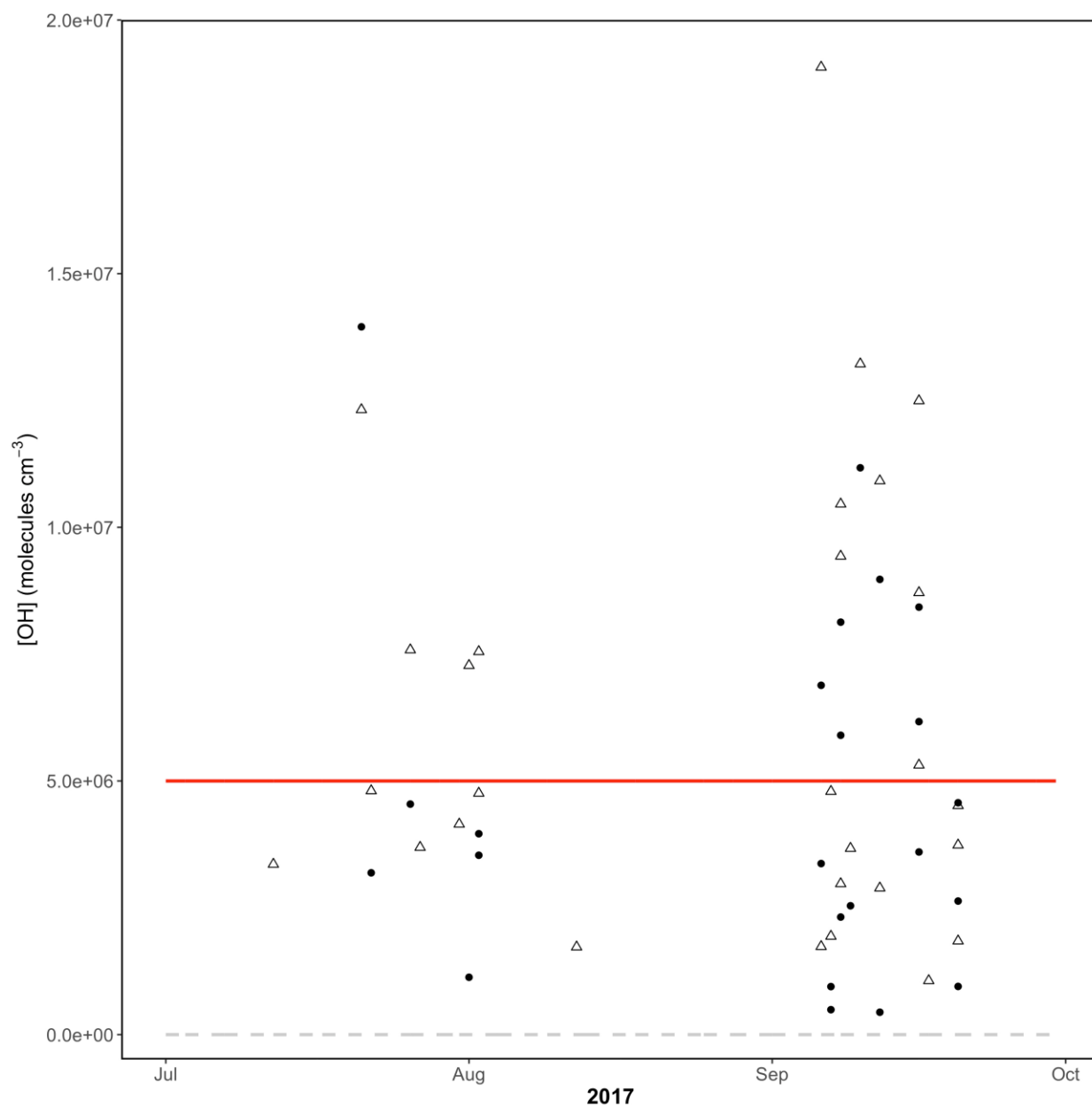


Figure 6. Estimated OH concentrations over Cape Town based on source emission ratios from FS (closed circles) and PD (open triangles). The red line represents a concentration of 5×10^6 molecules cm^{-3} .

As far as we can ascertain the OH concentration estimates presented here are the first for Cape Town and the surrounding Cape Peninsula. These results may assist with our understanding of

some of the air quality problems experienced in Cape Town.⁵⁶ In common with other large cities, pollutants from industrial and vehicular sources (e.g. PM_{2.5}, NO_x, SO₂, and VOCs) give rise to an atmospheric pollution phenomenon locally referred to as ‘brown haze’.⁵⁷ The ‘brown haze’ is particularly common in winter in a low-lying area known as the Cape Flats, a south eastern suburb of Cape Town, and is clearly visible from elevated positions. It is not surprising that the ‘brown haze’ is most noticeable in winter, as these pollutants are reduced by atmospheric oxidants e.g. O₃ and OH produced in the atmosphere in the presence of sunlight, which is at a minimum during winter. Furthermore, the synoptic climatology of Cape Town results in the formation of a strong inversion layer during winter, which traps emissions in the boundary layer / lower troposphere.

The Cape Point O₃ mole fractions displayed a mean of 32.9 ± 7.2 ppb during the sampling period.³⁵ The Cape Point Atmospheric Watch station is situated in the extensive Table Mountain National Park, which is recognized as one of the most botanically biodiverse regions in the world.⁵⁸ Therefore, the impact of biogenically derived reactive VOCs (e.g. isoprene) on OH, emitted from the surrounding diverse ‘fynbos’ plants into the atmosphere above the Cape Peninsula cannot be overlooked. Previous studies have found that under high isoprene/low NO_x conditions a significant discrepancy between measurements and model estimates of OH concentrations can be found.⁵⁹ Isoprene might also initiate OH re-cycling reactions, resulting in an increased removal of benzene and toluene from the atmosphere.^{38,60-63}

CONCLUSIONS

This study represents the first investigation of the correlation of the T/B ratios between two sampling sites in the city of Cape Town with Cape Point and a subsequent estimation of the OH concentrations in the atmosphere above the Cape Peninsula. The two urban sites of Cape Town,

the Foreshore (FS) and Potsdam (PD) displayed differing dominant emission sources of benzene and toluene into the atmosphere. Vehicular traffic was proposed as the dominant emission source of benzene and toluene at FS. Conversely, local industrial processes dominated the emission of these two compounds into the atmosphere at PD. The benzene and toluene observed at Cape Point displayed a clear source to the northeast, coincident with the city of Cape Town. Proposed direct intrusions of Cape Town air at Cape Point increased the benzene and the toluene mole fractions five-fold above the mean. The atmospheric OH radical concentrations were estimated for the Cape Peninsula from differences in T/B ratios between either FS or PD and Cape Point (assuming a nine-hour transit time at an average temperature of 290 K) with mean OH concentrations of 5.4×10^6 and 7.4×10^6 molecules cm^{-3} , respectively over the period of July-November 2017. Further work is required to refine this estimate, but, the results presented here begin to show the state of the air quality in Cape Town, during two seasons in 2017.

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ASSOCIATED CONTENT

Supporting Information

The Supporting information is available free of charge on the ACS Publications website at DOI:

Additional materials and results, temperature dependence of photochemical clock equation, complete timeseries of benzene, toluene and T/B ratios at the Foreshore, Potsdam and Cape Point, elevated mole fractions at FS and PD, analysis of T/B ratios using the NAME model (PDF), Analysis of daytime vs night time OH concentrations.

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Notes

The authors declare no competing financial interest. Supporting data are included as seven figures in Supporting Information file; any additional data can be obtained from the authors upon request (brett.kuyper@gmail.com).

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